"STUDIES ON THE CONDUCTING POLYMER OF 8 – HYDROXY QUINOLINE"

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ABSTRACT

8– Hydroxyl quinoline during chemical peroxidation catalysed by Cu2+ undergoes simultaneous polymerization and Oxidation. The polymer is characterized by chemical analysis, solution viscosity, Infrared and UV- visible spectra. UV-visible spectra indicate the presence of a band due to π-π* transition and an exciton band due to interband transition. The temperature dependence of electrical conductivity is used to understand the conductance mechanism which is found to 'grain' charge from state to state, also TGA is studied for thermal stability and thermal fragmentation.

KEYWORDS: 8– Hydroxyl Quinoline, Oxidation, Conductance, Grain & Fragmentation

INTRODUCTION

The research on highly conducting polymers has increased exponentially in the last twenty years[1]. All polymers become conducting upon "doping" with an oxidizing or reducing agent[2-3]. But it is not the electrical conductivity alone, which makes polythiophene[4], polypyrrole[5], polyaniline[6], polymers technologically interesting. The properties of the undoped and then semiconducting polymers also lead to important practical applications. With some linguistic licence, the fields of application of these polymers can be headed[7] by the "fourbig L's." L_1 : Electrical Conductivity; L_2 : Luminescence and non-linear optics; L_3 : Localisation; L_4: Large scale electronics. Conductivity, Luminescence and localization are closely related to the conjugated double bonds, which are characteristic of the structure of these polymers[8].

Recent research and development activities show that conducting polymers exhibit conductivity from the semiconducting range 10^{-5} s/cm right up to metallic conductivity 10^4 s/cm. with this range of electric conductivity. New applications are emerging for these modern electronic materials[9]. Polymers containing five and six member heterocycles bonded by single bonds or condensed with other cycles related to high molecular weight compound with improved heat resistance and thermostability. The aforementioned polymers could be prepared due to the work of V.V. Korshak[10] and other researchers stille etal[11] have evidently studies on derivative of polyquinolines.

In general, they are prepared by the oxidative polymerization[12] and electrochemical polymerization[13-14], were the methods to produce these polymers. The oxidation of various hydroxyl and amine functionalized quinoline monomers, 8 – hydroxyl quinoline[15] and 8 – amino quinoline[16], were studied in various polymerization medium. Electrospinnig is currently regarded as one of the most promising nanotechnologies for the preparation of fibers with micro and nanoscale diameters and a large specific surface area, which is a prerequisite for the attainment of high effectiveness in a number of applications e.g.medicine agriculture[17,19]. 8-hydroxyquinoline and its derivatives manifest antibacterial and antifungal activities [20,21]. The combination of water soluble polymers and 8-hydroxyquinoline derivatives result in the obtaining of a stable solution with antifungal activity suitable for

applications in agriculture [21].

EXPERIMENTAL

Preparation of the Polymer

0.0134 mol 8 – hydroxyl quinoline and 0.01 mol perchloric acid were, mixed in 25 ml acetonitrile. The mixture was cooled. To this mixture 10 ml of 0.556 m aqueous solution of ammonium persulphate containg 0.05 g of copper sulphate was added dropwise while sturring the solution in an inert atmosphere (N_2 gas was passed continuously during polymerisation). The mixture was diluted and filtered. The solid power obtained after filteration was dried in hot air oven.

METHOD

Elemental Analysis

The C, H and N analysis of all polymer sample was done by microestimation technique by using CARLO ERBA STRUM DP 200 at Center Drug Research Institute, RSIC, Lucknow.

Solubility

Solubility is one of the important parts of polymer characterization as it is the function of molecular weight, crystallinity and physical state. 0.1g of polymer sample was taken in test tube and 10 ml solvent was added to it. The solution was kept for 24 hours to note the solubility.[22,23]

Intrinsic Viscosity

Viscosity of the as prepared polymer were measured by an ubbelhode dilution viscometer at 28°C at different Concentration in DMSO, DMF, NMP, Acetone as solvents. In case poly (8–hydroxyl quinoline), the suggested transformation results in approximately uniform error distribution and renders extrapolation feasible [η] by usual graphical method = 0.065 dlg^{-1} and by refine graphical method [η] = 0.07 dlg^{-1}.

Electrical Conductivity Measurements

Polymer sample pallets were prepared by pressing the powder in a steel die by a hydrolic press under 5 metric ton/cm^2 pressure. The powder sample pallets were used for electrical conductivity measurements using a Systronics Direct Reading LCR Bridge model 926 as a function of temperature at a heating rate 1 Kmin^{-1} measured capacitance and resistance at 1 KHz was converted as dielectric constant, dielectric loss and conductance using cell dimensions.

U.V. – Visible Spectra

U.V. – Visible spectra of polymer were recorded in D.M.F. Solution using UV-240 Shimadzu Automatic recording double beam spectra photometer at room temperature in the range 190-700nm.

Infra Red Spectra

Infra Red Spectra were recorded on a perkin – Elmer 577 Spectrophotometer using KBr pellet technique at CDRI, Lucknow, India.

Thermal Gravimetric Analysis

The thermal gravimetric analysis was carried out on Perkin – Elmer TGS$_2$ Thermal analyser system in nitrogen atmosphere at Regional sophisticated Instrumentation Centre, Nagpur University with a heating rate 15 K min^{-1}.

RESULTS AND DISCUSSIONS

Elemental Analysis

The elemental analysis of the polymer gave C=47.48% (44.14%); H=2.88% (2.45%); N=6.08% (5.72%) for poly (8 – hydroxy quinoline) perchlorate respectively. The theoretical value (in bracket) have been calculated for poly (8 – hydroxyl quinoline) by considering monomer unit with one counter ClO_4^- ion. The presence of counter ion ClO_4^- was confirmed by perchlorate test[24.]

Infra Red Spectra

The IR absorption spectra of Chemically Synthesised Poly (8 – hydroxyl quinoline) with four strong bands at 1320, 1240, 1150 and 1030 cm^{-1} which are the characteristic of doped poly (8 – hydroxyl quinoline). The band at 740 cm^{-1} is attributed off out of poly disubstituted 2, 7 of 8 – hydroxyl quinoline. The bands due to the perchlorate ion are at 1100 and 615 cm^{-1} although the former band is masked by the doped 8 – hydroxy quinoline band. The ClO_4^- anions shows a high reduction potential and may undergo reactions to produce Cl^- ion.[25] The band due to ClO_4^- anion is at 615 cm^{-1}. These Cl^- ions may them in turn, react the polymer resulting in partially ionic, covalent or as ClO_4^- species in the polymer depends on the monomer as well as the perchlorate used. The OH stretching band are show at 3420 cm^{-1} which will be aromatic substituted group. The C-N stretching band was shown on the wavelength 1445 cm^{-1}. The C = N band are observed on the wavelength 1650 cm^{-1}.

Intrinsic Viscosity

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UV – Visible Spectral Analysis

The UV – visible Spectra for poly (8– hydroxy quinoline) perchlorate has been investigated in different solvents in order to indentify the band. The UV – visible Spectra are shown in fig 1. And also different bands are recorded in table 1. The absorption spectra are characterized by at least two bands in different solvents. The 370-390 band is assigned by π - π* transition. In this transition, the dipole moment on excitation will be larger than the ground state and will cause a hypsochromic shift in a solvent of higher dielectric constant, as observed from table 1.

Table 1: UV- Visible Data for the Poly (8 – Hydroxyl Quinoline) Perchlorate in Different Solvents.

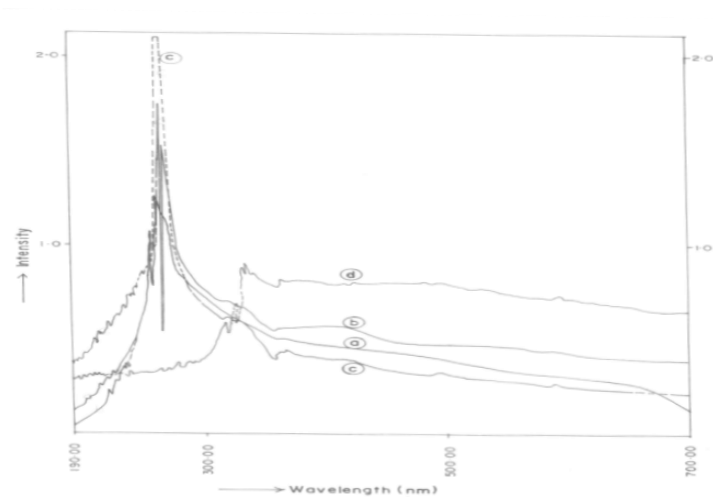| Solvent (Dielectric Constant)	λ max. (nm) (ev)	Transition
• DMSO • (46.68)	360 (3.45) 660 (1.88)	π – π * (Band Width) (Exciton band)
• DMF • (36.71)	320 (3.88) 420 (2.96) 590 (2.1)	π – π * (Band Width) – (Exciton band)
• NMP • (32.0)	320 (3.88) 370 (3.36) 490 (2.54) 590 (2.1)	π – π * (Band Width) – – (Exciton band)
• d) Acetone • (20.7)	360 (3.45) 420 (2.96) 480 (2.59) 590 (2.1)	π – π * (Band Width) – – (Exciton band)

FIG. **1** - UV Visible Spectra of Poly (8-hydroxy Quinoline) percolate in a) DMSO, b) DMF, c) NMP, d) acetone solvent.
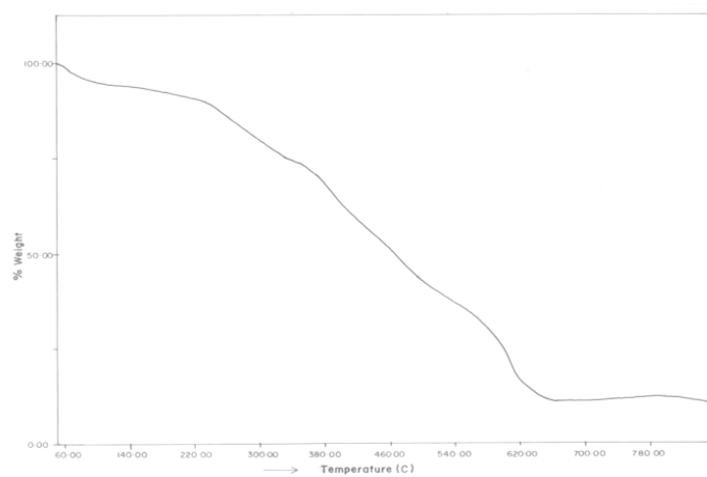

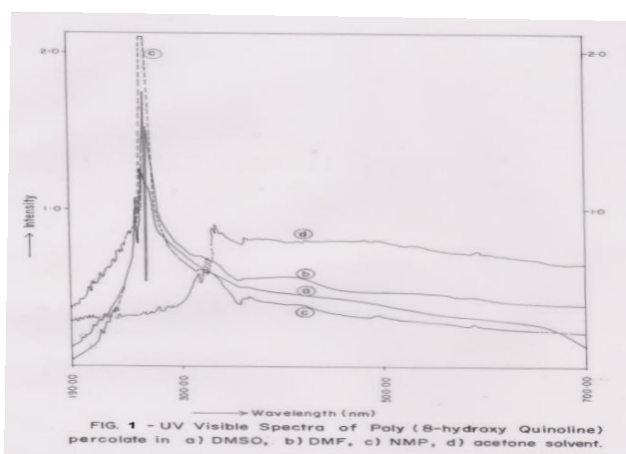FIG. **2** — TG THERMOGRAM OF POLY (8-hydroxy quinoline) perchlorate

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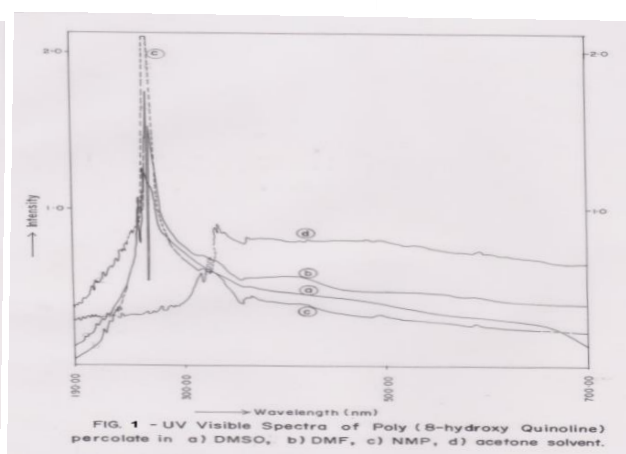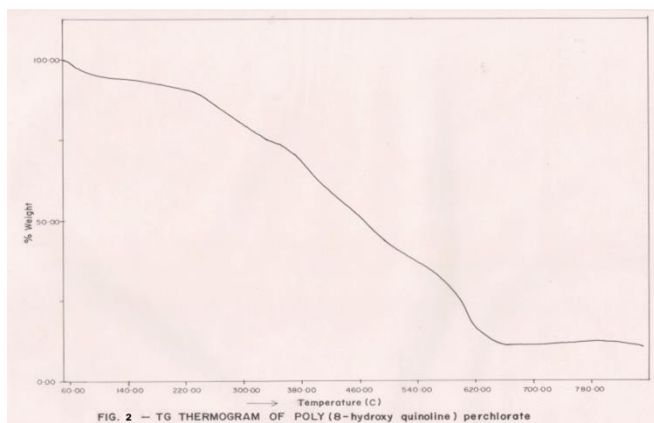

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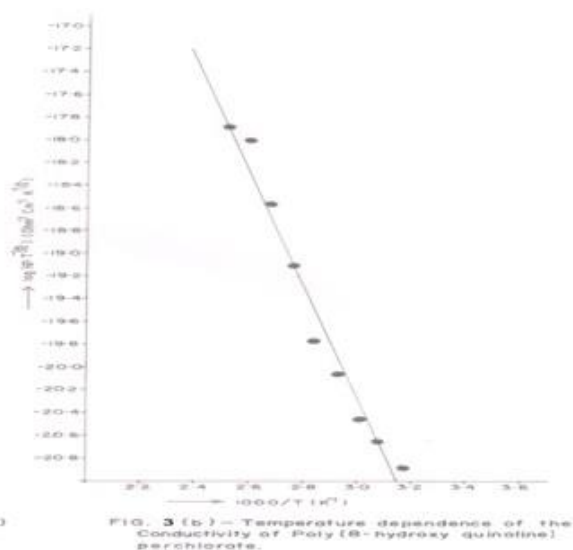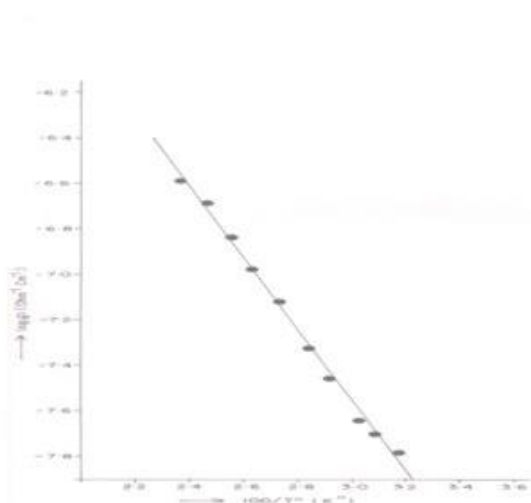
Thermal Gravimetric Analysis

TGA of the polymer sample of poly (8 – hydroxy quinoline) in Fig. 2; in nitrogen atmosphere shows that the mass loss starts at 60 °C and continuous upto 460 °C (51.39% mass loss) in the next stage mass loss occurs in the temperature range from 460 °C to 660 °C. The initial mass loss in the temperature 60 °C to 460 °C may be due to the conversion of counter ClO_4^- ions to Cl^- and the pyridine ring which have (4C, 1N, 3H) atom will give 50.29% mass loss. The mass loss from 460 – 660 °C is due to the inert atmosphere. The activation energy of thermal decomposition in inert atmosphere is **20.29 KJ/mole** from the TG data in inert atmosphere by using the Sharp – Wentworth method.[26]

Electrical Conductivity

The temperature dependence of the electrical conductivity data in the middle range of temperature fit the Arrhenius type equation (1)

$$\sigma(T) = \sigma_0 \exp^{(-Ea/2KT)} \tag{1}$$

In the temperature range investigated. The measured values are plotted semilogarithmically as a function of the reciprocal of temperature in ^{0}K as shown in figure.3

FIG. 3 (a) — Conductivity of Poly (8–hydroxy quinoline) perchlorate as a function of temperature

FIG. 3 (b) — Temperature dependence of the Conductivity of Poly (8–hydroxy quinoline) perchlorate.

In poly (8 – hydroxy quinoline) the activation energy of conductivity is **4.15 x 10^{-4}** e.v. &

σ $^{(T)}$ = **8.49 x 10^{-2}** ohm^{-1} cm^{-1}. In order to understand mechanism of conduction over the entire range of temperature, the temperature dependence charged species in solids. By analyzing the data, it is found that in the entire temperature range, the electrical conductivity can be expressed as

$$\sigma (T) \propto \exp^{(-T_0/T)^{1/2}} \tag{2}$$

Thus, when ln σ (T) is plotted as a function of T$^{-1/2}$ the data fitted to a straight line as shown in fig. 3(b). Poly (8 – hydroxy quinoline), where the substituent groups are electron withdrawing groups, the conductivity and activation energy of conduction less by factor of about 10 as compared to electron 'donating' groups such as hydroxyl group present in the chain[27], the mechanism of conduction in these polymer through grain barrier conduction; hopping conduction and tunneling conduction were considered accordingly.[28-31]
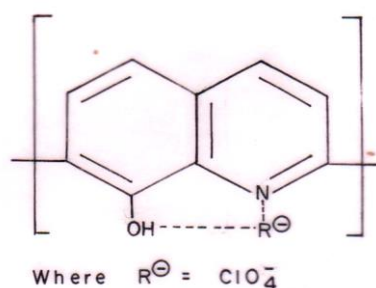
$$\ln (\sigma / T^{1/2}) \text{ Vs } 1000/T \tag{3}$$

$$\ln (\sigma / T^{1/2}) \text{ Vs } T^{-1/4} \tag{4}$$

$$\text{and } \ln \sigma \text{ Vs } 100/T^{-1/2} \tag{5}$$

Were plotted linear plots are obtained as shown in figure 3 (b) for the grain boundary barriers mechanism. Thus the conduction in these polymers may be predominantly by a grain boundary barriers. The presence of an electron withdrawing group in chain decreases the probability of grain boundary barriers.

CONCLUSIONS

The result of Chemical analysis and thermal gravimetric analysis indicate the more correct formula of poly (8– hydroxy quinoline) perchlorate as [C$_9$H$_7$NO]. ClO$_4$$^{-}$ and the structural unit may be as below.

Where R$^{\ominus}$ = ClO$_4^-$

poly (8 – hydroxyl quinoline) the linear chain polymer in which each (8 – hydroxyl quinoline) connected with one counter ion ClO$_4$$^{-}$. Which have withdrawing groups in the chain decreases the probability of grain boundary barriers.

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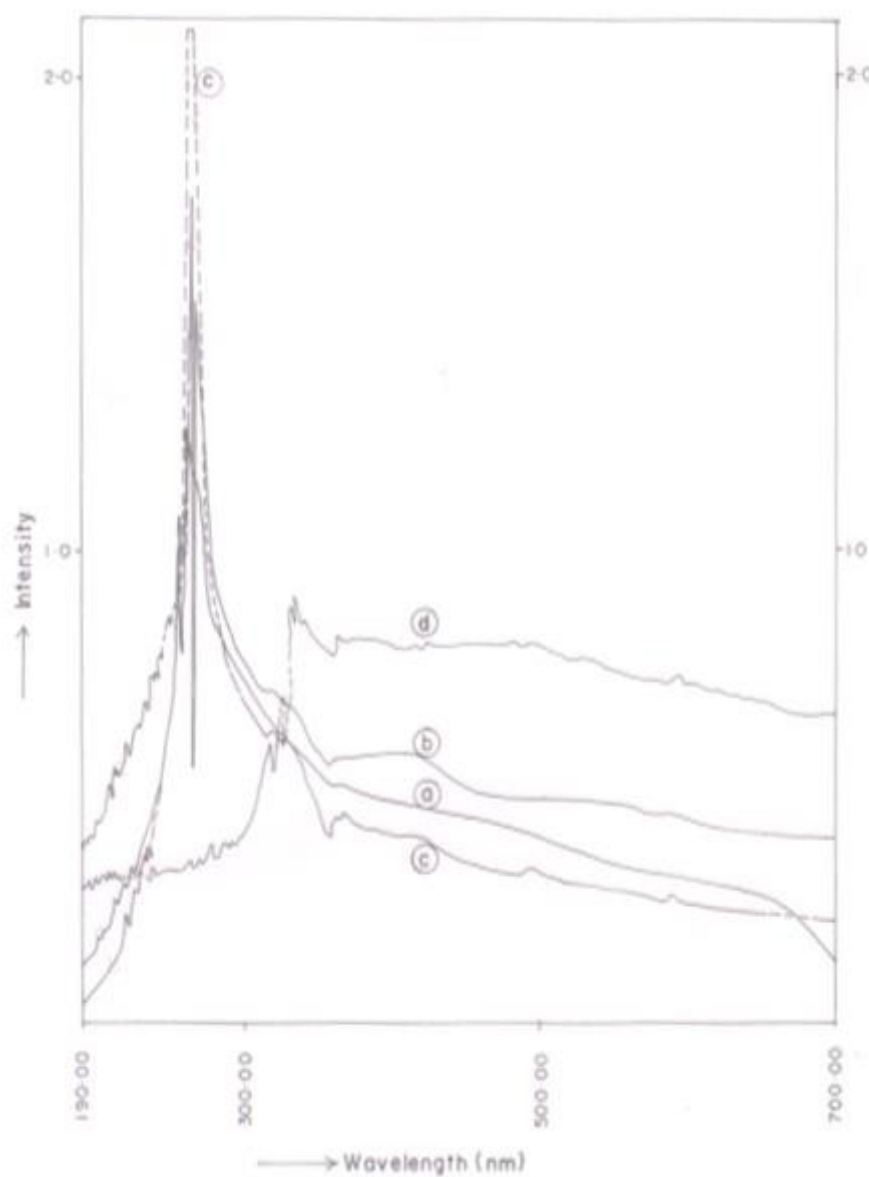
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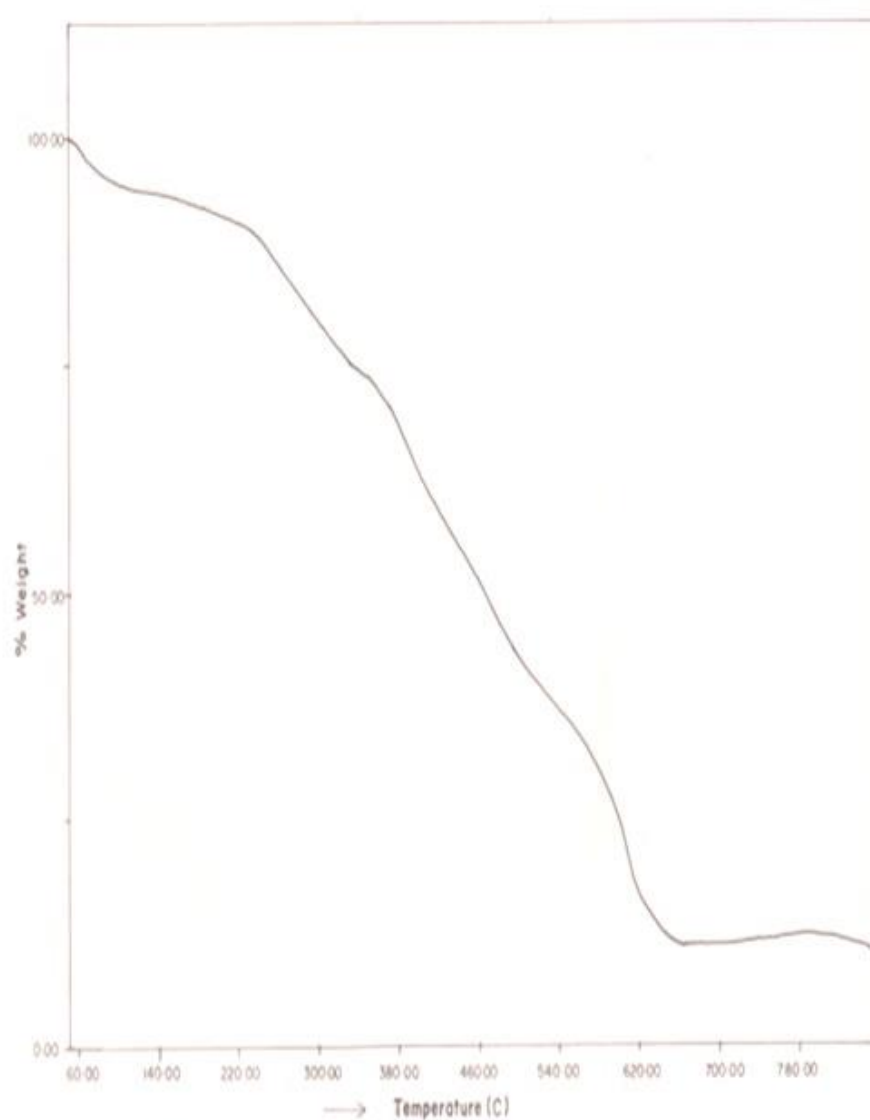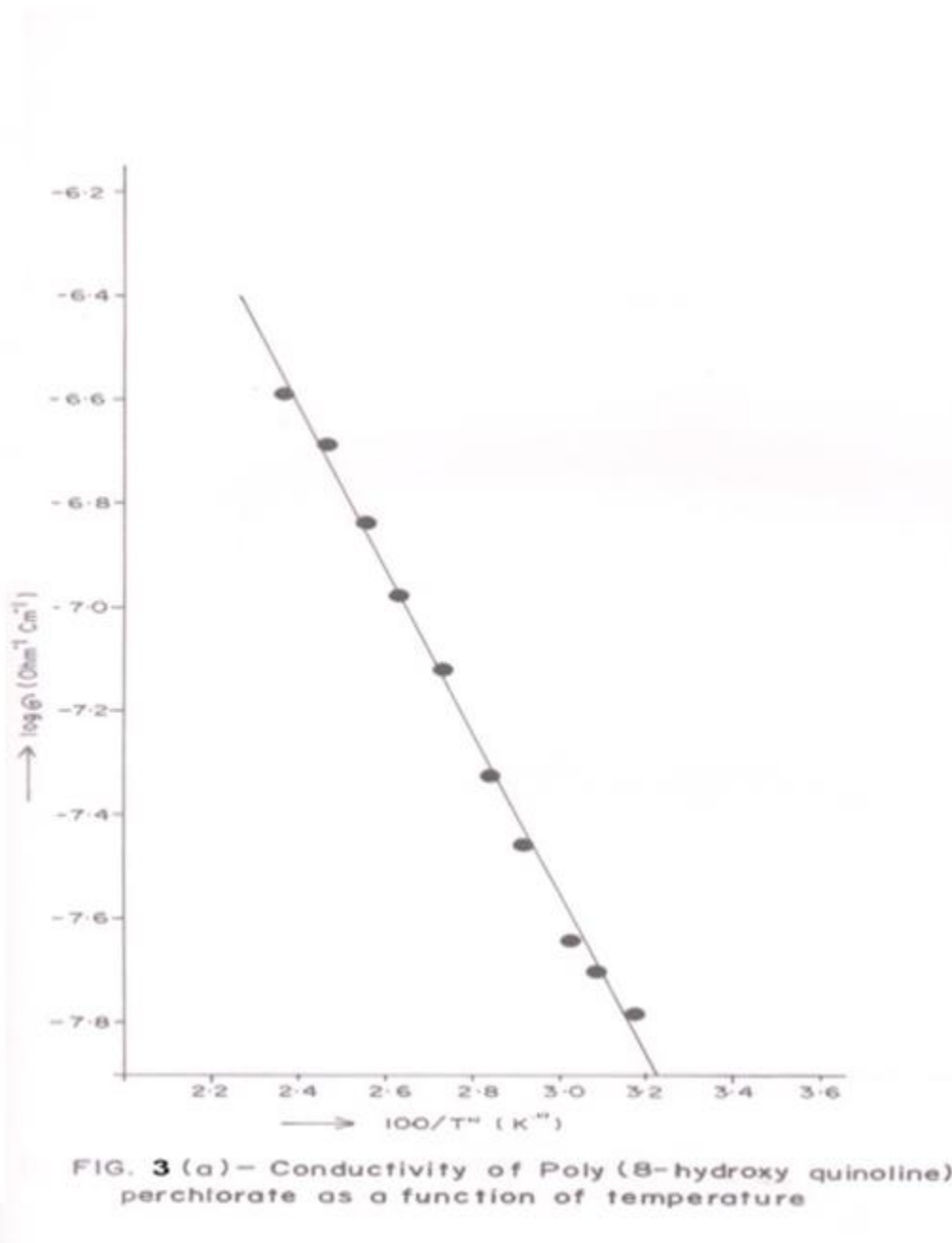
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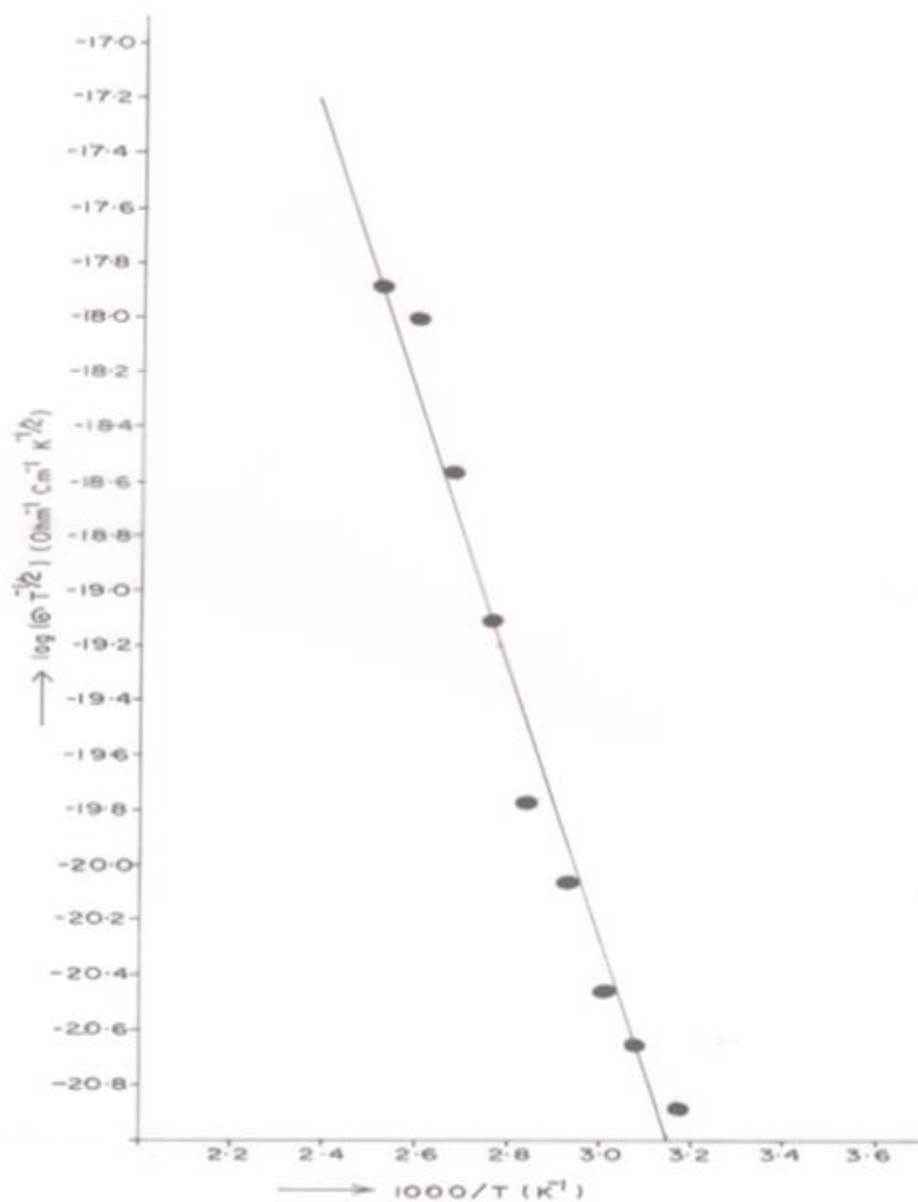FIG. 3 (a) – Conductivity of Poly (8-hydroxy quinoline) perchlorate as a function of temperature

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